

Concerning the research article:

**Methane sulfonic acid enhanced formation of molecular clusters of sulfuric acid  
and dimethyl amine**

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**Letter to the editor:**

In this document, we summarize the changes made in the revised manuscript to accommodate the requests and comments of the referees. The referee comments are reproduced fully in blue, our replies are in black, and the manuscript changes are highlighted in red.

We believe that we have answered all comments fully and that the corresponding manuscript changes have strengthened the conclusions and readability of the manuscript significantly. We therefore argue that the manuscript should be suitable for publication in Atmospheric Chemistry & Physics.

On behalf of all authors,



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## Reply to referee #1:

In this paper, the authors quantify how MSA impacts H<sub>2</sub>SO<sub>4</sub>+DMA nucleation rates using quantum calculations and the ACDC model. They show that MSA may increase nucleation rates by up to 300% in cold regions. These results are useful for the aerosol microphysics community. The paper is very well written and is commendably concise yet complete. I recommend publication after some minor comments are addressed; however, I am not an expert on the quantum chemical methods presented here, so other reviewers will be necessary to judge these methods.

P18681 L13: “MSA concentrations \*were\*”. In this sentence are you referring to gas- phase or particle-phase concentrations?

This sentence refers to gas phase MSA which will be clarified:

Introduction:

“In a recent study by Dall’Osto et al. (2012), gaseous MSA concentrations were found to decrease during marine particle formation events”

Figure 4: Would it be possible to make the arrow width proportional to the percentages in the table? I realized this would require 2 panels in order to get the 2 MSA concentrations, but this would be useful for visualizing the growth. It’s taken me some time to mentally map the table numbers onto the plot.

We agree that Figure 4 is somewhat demanding and we did find this suggestion interesting. However, we were unable to construct a 2-panel plot appearing simple and visually appealing wherefore we were forced to abandon this idea. In stead, the original version of Figure 4 was modified to highlight the main growth pathways, thereby assisting the reader in mapping the numbers onto the plot. The figure caption will be modified as well, as seen below.

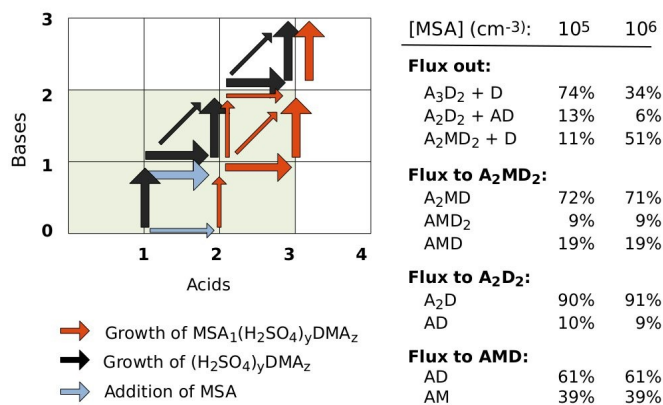


Figure 4. Main cluster formation pathways at T = 258 K and [H<sub>2</sub>SO<sub>4</sub>] = 10<sup>6</sup> molecules cm<sup>-3</sup>, [DMA] = 10<sup>8</sup> molecules cm<sup>-3</sup> and two representative MSA concentrations. Dominating growth pathways are indicated by thick arrows. Fluxes to clusters formed via several different pathways are indicated in the side table where A, M and D is shorthand H<sub>2</sub>SO<sub>4</sub>, MSA and DMA, respectively.

P18690 L22 and throughout: “DMA in most locations is in large excess compared to acid”. Is this representative of the remote marine boundary layer or the remote free troposphere (where DMS, the MSA precursor, may have been transported out)? Are the assumed DMA concentrations in the paper

representative of these locations? The authors should be sure they are not mixing continental DMA concentrations with remote MSA concentrations.

We are fully aware that, typically, continental DMA concentrations are significantly higher than marine DMA concentrations due to emissions from livestock and industry. We mainly base our choice of DMA levels on two reviews by Gibb et al (Global Bio-geochem. Cy., 13, 161-178, 1999) and Ge et al (Atmos. Environ., 45, 524-546, 2011), where typical marine concentrations of  $10^7$  to  $10^9$  molecules per  $\text{cm}^{-3}$  are reported. We acknowledge that DMA concentrations could be very different in the free troposphere but, to the best of our knowledge, no altitude resolved DMA measurements have been published. In the revised manuscript we will stress that conditions in the free troposphere are poorly known and that insight into atmospheric processes from our study is limited by this.

In section 3.2:

“We used three DMA concentrations spanning most reported marine values ( $y = 10^7$ ,  $10^8$  and  $10^9$  molecules  $\text{cm}^{-3}$ ) (see Gibb et al., 1999 and Table 4 in Ge et al., 2011). Only field data from the boundary layer is available and the results presented here may thus not be representative for the free troposphere, if DMA concentrations turn out to be very different from the boundary layer.”

and further in the conclusions:

“This is a consequence of MSA being a strong acid, binding strongly to DMA and  $\text{H}_2\text{SO}_4$ , and that DMA in most pristine oceanic locations is in large excess compared to acid.”

## Reply to referee #2:

The authors apply a kinetic model (ACDC) and quantum chemical calculations to study the contribution of gaseous MSA to cluster formation, with and without the presence of dimethyl amine (DMA) and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) molecules. Like referee #1 I am not an expert on these methods. However, I find the present paper somewhat incomplete and would like to see appropriate revisions made. My specific comments are as follows:

1. The authors do not consider hydration, i.e. the potential effect of H<sub>2</sub>O molecules and associated ligand formation on the overall contribution of MSA to stabilization and growth of clusters. At least one more paragraph and figure should be dedicated to this mechanism to provide a more realistic evaluation (see also their comment on postponing calculations for larger clusters to later work in their Conclusions).

We acknowledge that, under atmospheric conditions, the clusters are likely containing one or more water molecules and we agree that this effect should be discussed. However, obtaining the actual free energies for each hydrated cluster requires vast computational effort, due to increased need of configurational sampling and increased expense of each electronic structure calculation.

However, while water is known to stabilize pure acid clusters strongly, its effect on clusters containing DMA is likely much less significant. As DMA is a much stronger base than water it is unlikely that water will break any of the DMA-MSA bonds, but more likely that water will add to the existing clusters by forming new hydrogen bonds. Thus, the main formation pathways and formation rates are likely not significantly affected by hydration. This hypothesis is supported by some recent publications investigating this effect in detail, e.g. Henschel et al (2014).

This additional paragraph has been added to the introduction:

"The clusters studied in this work do not contain water molecules due to the considerable additional computational effort required to obtain the necessary thermodynamic data. Hydration can be expected to stabilize weakly bound clusters more than strongly bound clusters and it is therefore conceivable that we will underestimate the contribution from some of the minor growth pathways. However, since DMA is a much stronger base than water, hydration is not likely to have a significant effect on the stability of clusters containing DMA. Therefore, the main growth pathways and growth rates are unlikely to change significantly due to hydration. See e.g. Almeida et al (Nature, 502, 359-363, 2013) and Henschel et al, (J. Phys. Chem. A, 118, 2599–2611, 2014) for further discussion."

2. Again, in the Conclusions the authors state that "The formation mechanism of MSA rich aerosols thus remains unknown". However, they have completely missed previous studies showing that DMS oxidation pathways via DMSO and MSIA produce MSA, in particular at lower temperatures and NO<sub>x</sub> levels (see, e.g., Davis et al., J. Geophys. Res., 103, 1657,1998; Barnes et al., Chem. Rev., 106, 940, 2006). At least one more paragraph needs to be included to consider these (additional) sources of MSA.

We are completely aware of the extensive literature on the formation mechanisms of MSA from DMS. The sentence: "The formation mechanism of MSA rich aerosols thus remains unknown" only relates to the formation of aerosols from a pre-existing pool of MSA (surely formed from DMS as the referee states). We will rephrase this sentence in the revised manuscript to avoid misunderstandings.

In the conclusions:

“At present, we are unable to explain MSA/H<sub>2</sub>SO<sub>4</sub> ratios up to 30 % observed by Ayers et al. (1991), Huebert et al. (1996) and Kerminen et al. (1997) in small aerosol particles, but we have shown that MSA may enter the aerosol particle at the earliest possible stage and significantly assists in cluster formation”

3. Section 2.2: Only one value (without uncertainty range) has been adopted (from DalMaso et al.) for the condensational loss rate to preexisting particles. In view of the large uncertainties in the evaluation of such loss rates (up to at least a factor of 2, based on CN > 3 nm diameter particle measurement uncertainties alone), a rigorous uncertainty analysis needs to be included and also shown in Figs. 2 and 3. This error source has large implications for all of the following calculations and conclusions.

We acknowledge that the condensational sink is associated with substantial uncertainty. We have conducted the requested uncertainty analysis and have found that the value of the condensational loss rate has a modest, although noticeable effect on the ratio of the particle formation rates. The figure below shows the effect on  $r_2$  and  $r_3$  from varying the condensation sink from  $10^{-3} \text{ s}^{-1}$  to  $5 \times 10^{-3} \text{ s}^{-1}$ , i.e. about a factor of two around the used value of  $2.6 \times 10^{-3} \text{ s}^{-1}$ . These findings will be discussed in the revised manuscript and the figure will be included as supporting information.

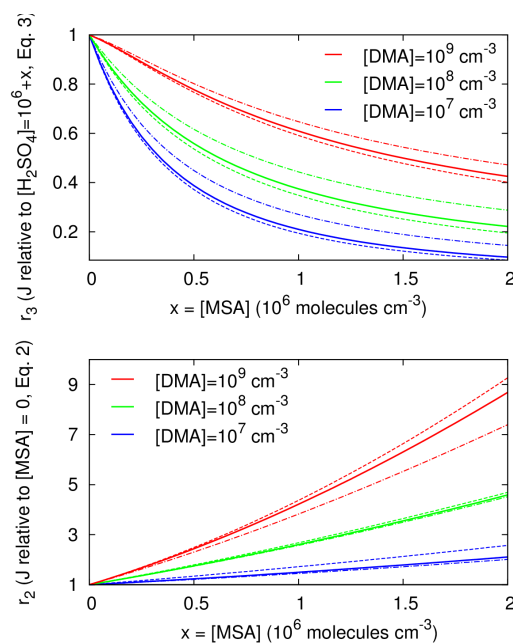


Figure S1: Plots of  $r_2$  and  $r_3$  ( $[\text{H}_2\text{SO}_4]=10^6 \text{ cm}^{-3}$  and  $T=258 \text{ K}$ ) at varying concentrations of DMA and varying values of the condensational loss rate of particles due to pre-existing aerosols. The loss rates are  $10^{-3} \text{ s}^{-1}$  (dotted lines),  $2.6 \times 10^{-3} \text{ s}^{-1}$  (solid lines) and  $5 \times 10^{-3} \text{ s}^{-1}$  (dash-dotted lines).

In section 2.2:

“An external sink with a loss rate coefficient of  $2.6 \times 10^{-3} \text{ s}^{-1}$ , corresponding to coagulation onto pre-existing larger particles is used for all clusters (Dal Maso et al., 2008). Testing showed that variations in this value between  $10^{-3} \text{ s}^{-1}$  and  $5 \times 10^{-3} \text{ s}^{-1}$  did not affect the main conclusions of this study (Figure S1).”

Further comments:

p. 18682, line 16: What are the typical uncertainties / limitations / inaccuracies of these "popular" methods? Discuss this and add at least one reference.

It is very difficult to predict uncertainties for untested systems wherefore a thorough benchmarking is conducted (results presented in Tables 1 and 2). Following, much of Section 2.1 (p. 18683) is dedicated to this question, including also several references. In the revised manuscript, Section 2.1 will be adjusted to clarify this procedure.

“It is often mentioned that average uncertainties are on the order of 1 kcal mol<sup>-1</sup>, but depending on the specific system and method, uncertainties may be significantly larger. Therefore, careful testing and validation should precede each study, which we will discuss in the following.”

line 18: insert: ...is "considered" one of the...

Section 2.1: Corrected

p. 18686, line 19: Explain this "surprise".

It is well known that strong acids and bases tend to form stronger hydrogen bonds and hence form more stable clusters. In terms of pK<sub>a</sub>, MSA is a weaker acid than H<sub>2</sub>SO<sub>4</sub>, wherefore we would expect that the H<sub>2</sub>SO<sub>4</sub> dimer was stronger bound than the MSA-H<sub>2</sub>SO<sub>4</sub> cluster and that the MSA dimer would be the weakest bound of these three systems. However, the opposite trend is observed which, to us at present, is surprising. This will be clarified in the revised manuscript.

Section 3.1:

“It is well known that strong acids and strong bases tend to form strong hydrogen bonds and more stable clusters than weaker acids and bases. Since MSA is a weaker acid than H<sub>2</sub>SO<sub>4</sub> it is expected that the MSA · DMA binding energy is weaker than the H<sub>2</sub>SO<sub>4</sub> · DMA binding energy (Table 2). It is, on the other hand, surprising that the MSA · H<sub>2</sub>SO<sub>4</sub> bond is at least 1.5 kcal mol<sup>-1</sup> stronger than the H<sub>2</sub>SO<sub>4</sub> · H<sub>2</sub>SO<sub>4</sub> bond, and that the MSA · MSA bond is at least 0.5 kcal mol<sup>-1</sup> stronger than the H<sub>2</sub>SO<sub>4</sub> · H<sub>2</sub>SO<sub>4</sub> bond.”